Dimethyl-(2-methoxy-1-naphthyl)-carbinol.—A solution of 2.16 g. of methyl 2-methoxy-1-naphthoate in 60 ml. of benzene was added dropwise to a Grignard reagent prepared from 3.7 ml. of methyl iodide and 1.22 g. of magnesium in 60 ml. of ether. The reaction mixture was heated under gentle reflux for 3 hours and poured into a mixture of ice and ammonium chloride. The organic layer and three ether extracts of the aqueous portion were evaporated in the cold. Crystallization of the residue from aqueous methanol containing a drop of concentrated ammonium hydroxide gave 1.33 g. (61%) of colorless crystals of the tertiary carbinol, m.p. 95–95.5°.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.82; H, 7.58.

Reaction of Methylmagnesium Iodide and 2-Methoxy-1-naphthoic Acid.—To the Grignard reagent prepared from 3.7 ml. of methyl iodide and 1.22 g. of magnesium in 80 ml. of ether was added a slurry of 2.02 g. of 2-methoxy-1-naphthoic acid in 50 ml. of benzene. After 20 hours of heating under reflux, the reaction mixture was poured into dilute hydrochloric acid. The organic layer was removed and the aqueous layer was extracted three times with ether. The combined organic layers were extracted three times with 10% aqueous sodium hydroxide. Acidification with concentrated hydrochloric acid caused the separation of 1.51 g. (80%) of a colorless precipitate melting at 123–128° with the evolution of a gas. Repeated crystallization of the material from aqueous acetone did not raise the decomposition point above 124–128° (slow heating). Ferric chloride in methanol produces a dark blue coloration with this compound, which was identified as 2-hydroxy-1-naphthoic acid. The decomposition point given in the literature is 124–128°.[25]

Anal. Calcd. for $C_{11}H_8O_3$: C, 70.21; H, 4.29; neut. equiv., 188. Found: C, 69.95; H, 4.47; neut. equiv., 188.

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[25] R. Schmitt and E. Burkard, *Ber.*, **20**, 2699 (1887).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Diels–Alder Reactions of 9-Substituted Anthracenes.[1] II. 9-Cyanoanthracene

BY JOHN S. MEEK, JOHN R. DANN AND BING T. POON

RECEIVED DECEMBER 27, 1955

9-Cyanoanthracene has been found to give *ortho*-type adducts with acrylamide, methyl acrylate and acrylic acid. With allyl alcohol and acrylonitrile both possible isomeric adducts were found. The *ortho*-type adduct predominated with allyl alcohol while the major isomer was the *meta*-type with acrylonitrile.

When 9-anthraldehyde was condensed with acrylic acid, allyl alcohol and acrylonitrile only one of two possible isomeric adducts was isolated in each case.[2] These adducts were all 12-substituted ethanoanthracenes in which the carboxaldehyde group and the functional group coming from the dienophile were located on adjacent carbon atoms (*ortho*-type adduct) rather than on non-adjacent atoms (11-substituted ethanoanthracenes, *meta*-type adducts).

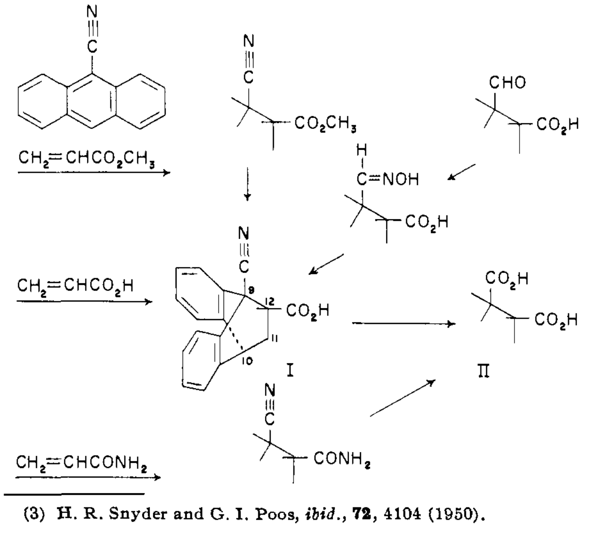
In the present work 9-cyanoanthracene was used as a diene and, with acrylic acid, methyl acrylate and acrylamide, only the *ortho*-type adduct was found.

With allyl alcohol the product was an oil which upon heating with acetic anhydride gave two crystalline acetates. The major acetate was again an *ortho*-type derivative and was formed in about twice the amount of that of the second acetate. Although the adducts of allyl alcohol were not isolated directly it is believed that their relative amounts correspond to those of the acetates and that heating with acetic anhydride did not cause any isomerization. To isomerize adducts which are positional isomers requires a complete reversal of the Diels–Alder reaction. All the adducts of 9-substituted anthracenes which we have so far examined are colorless and even when heated at melting points of above 200° they do not produce the yellow color characteristic of a 9-substituted anthracene.

When acrylonitrile was used as a dienophile both isomeric adducts were formed and the *meta*-type 11-substituted adduct predominated for the first time.

9-Cyanoanthracene can be considered the dibenz analog of the open chain compound *trans*-1-cyano-1,3-butadiene. This latter substance has been reported to give only *cis–ortho*-type adducts with methyl and ethyl acrylate and when condensed with acrylonitrile the adduct formed could not be separated from the dimer of 1-cyano-1,3-butadiene in sufficient quantity for characterization studies.[3] Incorporating the cyanobutadiene system into an anthracene derivative eliminated *cis–trans* isomerism in the adducts as well as dimerization of the diene and simplified our work.

The structure of the acrylic acid adduct I of 9-cyanoanthracene was proved by synthesizing the compound from the known 9-formyl-9,10-ethano-



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[1] This paper was presented in part at the XIIth International Congress of Pure and Applied Chemistry, September, 1951, and was supported by the Office of Naval Research.

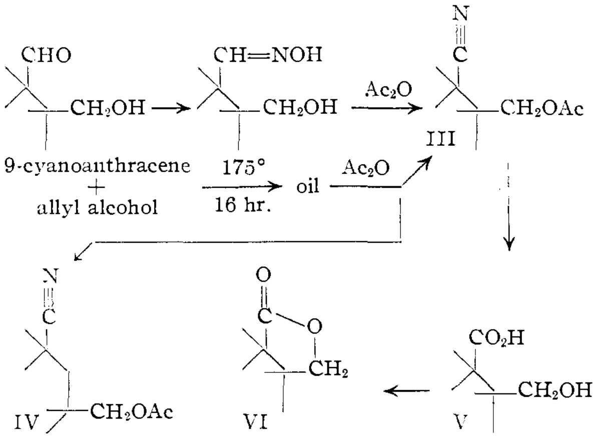
[2] J. S. Meek, B. T. Poon and S. J. Cristol, THIS JOURNAL, **74**, 761 (1952).

[3] H. R. Snyder and G. I. Poos, *ibid.*, **72**, 4104 (1950).

anthracene-12-carboxylic acid.[2] The methyl acrylate adduct was also converted to I by hydrolysis of the ester group. The acrylamide adduct on hydrolysis gave a dibasic acid II which melted at 270°. This same acid was prepared from I and therefore had the acid groups in the 9- and 12-positions.

The condensation of allyl alcohol and 9-cyanoanthracene gave an oil which could not be induced to crystallize. When this oil was refluxed with acetic anhydride two isomers, m.p. 98° (III) and 121° (IV), were obtained, both having the correct analysis for an acetylated adduct. When the *ortho*-type adduct of 9-anthraldehyde and allyl alcohol[2] was converted to its oxime and then refluxed with acetic anhydride the major isomer melting at 98° was produced. The higher melting isomer was therefore assigned the *meta*-type 9,11-substituted structure IV.

The structure of III was also shown by the fact that on hydrolysis a hydroxy acid (V) was formed which melted quite sharply at 155°, then solidified on further heating and melted a second time at 223°. Analysis of the new compound showed V had lost water and that a lactone VI had been formed. A similar phenomenon of a double melting point and lactone formation was encountered in our earlier work with the isomeric 9-methylol-9,10-ethanoanthracene-12-carboxylic acid which melted at 149°, solidified to the lactone on heating and melted again at 191°.[2] It is to be noted that in both cases the lactone melted higher than the corresponding hydroxy acid whose polarity may have been reduced by intramolecular hydrogen bonding.



The condensation of acrylonitrile and 9-cyanoanthracene gave two isomers, m.p. 167° (VII) and 205° (VIII). In one run VII predominated and in a second VIII was the major isomer. The lower melting isomer was identified as 9,12-dicyano-9,10-ethanoanthracene by its synthesis from the *ortho*-type adduct of 9-anthraldehyde and acrylonitrile, by its formation when the adduct of 9-cyanoanthracene and acrylamide was dehydrated, and by its hydrolysis to the dibasic acid II. The higher melting adduct was therefore assigned the 9,11-dicyanoethanoanthracene structure. Treatment of VIII with potassium hydroxide in ethylene glycol led to the dibasic acid, m.p. 270°. More recently this acid has been reported to be formed by condensing 9-anthroic acid with acrylic acid and by the condensation of the sodium salts of these acids.[4] These reactions did not lead to the isolation of any of the *ortho*-type adduct.

When 9-cyanoanthracene was refluxed with styrene and allylamine no adduct could be isolated.

Our present work indicates that there is a greater tendency to form *meta*-type adducts with 9-cyanoanthracene than with 9-anthraldehyde. Resonance effects should make the 10-position of the 9-cyanoanthracene positive as well as the β-carbon atoms of acrylic acid, methyl acrylate, acrylamide and acrylonitrile so that if polar effects were important one would expect *meta*-type adducts to form. This was observed only with acrylonitrile. Allyl alcohol due to resonance effects has a negative γ-position and if polar effects again were important one would predict formation of the *ortho*-type adduct. However, allyl alcohol gave a considerable amount of the *meta*-type adduct. The formation of *meta*-type adducts cannot be explained on the basis of steric factors minimizing *ortho*-type adduction since the minimum amount of *ortho*-type adduction was found with acrylonitrile which has the smallest functional group. These results are summarized in Table I.

Table I

Adducts of 9-Cyanoanthracene

Dienophile	Hr.	Conditions Temp., °C.	Adduct, % 9,12	9,11
Acrylic acid	2	135–140	21	..
Methyl acrylate	72	90 then		
	21	130–140	38	..
Acrylamide in xylene	16	125–130	25	..
Allyl alcohol	16	170–175	34	16
Acrylonitrile	18	135–145 then		
	22	190–200	18	33
	23	190–200	8	17

Experimental

9-Cyanoanthracene.—This was obtained by the method of Fieser and Hartwell[5] and melted at 178–179.5°.

9-Cyano-9,10-ethanoanthracene-12-carboxylic Acid.—One-half gram (0.0018 mole) of 9-formyl-9,10-ethanoanthracene-12-carboxylic acid, 1.00 g. (0.029 mole) of hydroxylamine hydrochloride, 10 ml. water and sufficient 5% sodium hydroxide to effect solution was permitted to stand 24 hours. It was acidified with hydrochloric acid and methanol was added to clarify the suspension. Slow evaporation of the methanol from the solution at room temperature gave 0.23 g. (45%) of oxime. The melting point was indefinite. With rapid heating it melted with bubbling around 95° and higher with slow heating.

Anal. Calcd. for $C_{18}H_{15}NO_3$: C, 73.70; H, 5.15. Found: C, 73.59; H, 5.27.

Twenty one-hundredths gram (0.00058 mole) of oxime was placed in a 10 × 75 mm. Pyrex test-tube, and the contents were heated for 0.5 hour at 135 to 139°. The crude material melted at 195 to 197.5°. Crystallization from Skellysolve C (petroleum ether, b.p. 85 to 100°)–benzene mixture gave 0.18 g. (90%) of material, m.p. 196–198°. A subsequent crystallization failed to raise the melting point. However, after drying in a vacuum over phosphorus pentoxide, the 9-cyano-9,10-ethanoanthracene-12-carboxylic acid melted at 210 to 212°.

Anal. Calcd. for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76. Found: C, 78.89; H, 4.86.

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(4) K. Alder and K. Heimbach, *Chem. Ber.*, **86**, 1312 (1953).

(5) L. F. Fieser and J. L. Hartwell, This Journal, **60**, 2555 (1938).

An attempt to convert the oxime to the cyano-acid using acetic anhydride in pyridine gave a white product, m.p. 166–167°, when recrystallized from benzene–Skellysolve B (petroleum ether, b.p. 60–70°). Analysis indicated it may have been the oxime-mixed acid anhydride and so it was not investigated further.

Anal. Calcd. for $C_{22}H_{14}NO_5$: C, 70.01; H, 5.07; N, 3.71. Found: C, 70.62; H, 5.13; N, 3.82.

A mixture of 2.75 g. (0.0135 mole) of 9-cyanoanthracene in 14.4 g. of glacial acrylic acid containing 0.1 g. of hydroquinone was heated under reflux at 135–140° for 2 hours. At this time the temperature in the reaction flask began to rise and the liquid appeared to be thickening so the heating was stopped. Upon cooling, 0.4 g. of yellow crystals were formed and removed. The reaction mixture was diluted with 125 ml. of water and then extracted with three 100-ml. portions of benzene. The benzene solutions were combined and extracted with a total of 90 ml. of 5% sodium hydroxide solution. Upon acidifying the sodium hydroxide solution with hydrochloric acid, a sticky white precipitate was formed. After crystallization from benzene, 0.8 g. (21%) of white granular crystals was obtained, m.p. 203–208°. A second crystallization gave a m.p. of 212–214° and the mixed m.p. with the acid prepared by dehydrating the oxime was not depressed.

Methyl 9-Cyano-9,10-ethanoanthracene-12-carboxylate.—A mixture of 4.0 g. (0.0197 mole) of 9-cyanoanthracene and 34 ml. (0.4 mole) of methyl acrylate containing 0.1 g. of hydroquinone was heated in a sealed tube at 90° for 72 hours, but upon cooling the tube the solution became almost solid with long, yellow needles resembling 9-cyanoanthracene. The tube was not opened but was heated again for 21 hours at 130–140°. The reaction mixture contained no crystals upon cooling in ice-water but yellow needles were observed when the tube was cooled in Dry-Ice and acetone. The tube was opened and the excess methyl acrylate was removed on the steam-bath. Upon dissolving the oily residue in methanol and cooling, a total of 2.2 g. (38%) of white crystals was obtained, m.p. 114–116°. Recrystallization from methanol raised the melting point to 115–116°.

Anal. Calcd. for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.61; H, 5.29; N, 4.75.

Two tenths of a gram (0.00069 mole) of the adduct of 9-cyanoanthracene and methyl acrylate was heated for 24 hours at 130° in 7 ml. of ethylene glycol containing 0.60 g. of potassium hydroxide. The reaction mixture was cooled, acidified with 50% hydrochloric acid and extracted with four 25-ml. portions of ether. The ether solution was then extracted with two 25-ml. portions of 5% sodium bicarbonate solution. The bicarbonate extract was acidified with hydrochloric acid and 0.13 g. of a light yellow precipitate was formed, m.p. 195–202°. Upon recrystallization from benzene 0.1 g. (53%) was recovered and the melting point was raised to 214–215°. The mixed melting points with the adduct of 9-cyanoanthracene and acrylic acid and the dehydrated oxime above were not depressed.

9-Cyano-9,10-ethanoanthracene-12-carboxamide.—A mixture of 2.03 g. (0.01 mole) of 9-cyanoanthracene, 2.8 g. (0.04 mole) of acrylamide, 0.1 g. of hydroquinone and 20 ml. of xylene was heated for 16 hours under a reflux condenser at 125–130°. Upon cooling, the entire reaction mixture was filled with a light yellow mass of crystals. These were filtered and heated on the steam-bath with 50 ml. of water to remove unreacted acrylamide. Upon recrystallization from methanol, 1.3 g. of yellow 9-cyanoanthracene was obtained plus 0.7 g. (25% conversion) of white crystals, m.p. 219–221°. A temperature of 140° for 19 hours in a sealed tube gave a 69% yield.

Anal. Calcd. for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.96; H, 5.38; N, 10.30.

9,10-Ethanoanthracene-9,12-dicarboxylic Acid.—A mixture of 2.0 g. (0.0073 mole) of the adduct of 9-cyanoanthracene and acrylamide, 1.12 g. of potassium hydroxide (0.02 mole) and 15 ml. of ethylene glycol was heated for 114 hours from 105–165° and the liberation of a slight amount of ammonia was observed throughout the entire period. After cooling, the thick dark yellow solution was extracted with 25 ml. of ether and 0.8 g. of a yellow oil was removed. The mother liquor was acidified with hydrochloric acid and extracted with four 25-ml. portions of ether. Upon evaporation of the ether, a yellow oil remained which could not be induced to crystallize from benzene, acetone or methanol. The oil was then dissolved in 5% sodium hydroxide solution and the precipitate formed upon the addition of hydrochloric acid was separated and dissolved in hot benzene. Upon cooling, 1.22 g. (56%) of white crystals was obtained, m.p. 207–212°. After recrystallizing again from benzene a melting point of 230–232° with bubbling was observed. The material was then dried at increasingly higher temperatures until a constant weight was finally obtained by drying over phosphorus pentoxide in a good vacuum at 112°.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79; neut. equiv., 147. Found: C, 73.54; H, 5.00; neut. equiv., 150.

This same acid was obtainable by a similar hydrolysis of the adduct of 9-cyanoanthracene and acrylic acid.

Adducts of Allyl Alcohol and 9-Cyanoanthracene.—A mixture of 6.09 g. (0.03 mole) of 9-cyanoanthracene, 34.8 ml. (0.6 mole) of allyl alcohol and 0.2 g. of hydroquinone was sealed in a glass tube and heated at 170–175° for 16 hours. The contents of the tube consisted of a clear, light brown liquid. Upon cooling in Dry Ice and acetone and opening the tube, no internal pressure was observed and only a small amount of flocculent precipitate was formed. This weighed 0.1 g. and was unreacted 9-cyanoanthracene. The excess allyl alcohol was distilled on a steam-bath leaving a residue of 8.5 g. of clear, light brown viscous oil. This oil could not be made to crystallize from ethanol, ethanol–water, or Skellysolve B so it was heated on the steam-bath with 20 ml. of acetic anhydride and 1 drop of sulfuric acid for 2 hours. Fifty milliliters of water was then added and the mixture was heated for 10 more minutes. It was then cooled in ice and 50 ml. of water was added and a dark oil separated. The aqueous layer was decanted and the oil was dissolved in 10 ml. of hot ethanol. After standing overnight, 8 g. (87%) of crude crystalline material had formed, m.p. 82–92°.

Upon recrystallization from ethanol it was noted that crystals of two different types were formed and that these had different melting points. One form (A) was in the shape of short thick needles and melted at 97–98°. The other crystals (B) were irregular globules which melted at 120–121°. By a process of repeated, slow recrystallizations from ethanol and by picking out different crystal types, the adduct was separated into two fractions: A, 3.10 g. (34%), m.p. 97–98°, and B, 1.5 g. (16%), m.p. 120–121°.

Isomer A, 9-cyano-9,10-ethanoanthracene-12-methylol acetate, was also prepared from the allyl alcohol adduct of 9-anthraldehyde.[2] One gram of the adduct, m.p. 171°, 1 g. of hydroxylamine hydrochloride, 5 ml. of pyridine and 5 ml. of absolute ethanol were refluxed for 9.5 hours. The mixture was cooled, poured into water and extracted with benzene from which 0.90 (85%) of oxime, m.p. 168°, was obtained. The analytical sample melted at 167.5–168.5°.

Anal. Calcd. for $C_{18}H_{17}NO$: C, 77.39; H, 6.14; N, 5.01. Found: C, 77.73; H, 6.23; N, 5.05.

One-half gram of this oxime was boiled for 20 minutes in 1 ml. of anhydrous pyridine and 5 ml. of acetic anhydride and allowed to stand for one hour in order to dehydrate the oxime group and acetylate the alcohol group. The material was poured into water and 0.54 g. (94%) of white crystals, m.p. 95–96°, was obtained which when mixed with isomer A above showed no melting point depression, but when mixed with isomer B, a m.p. of 70–90° was obtained. The analytical sample melted at 96–96.5°.

Anal. Calcd. for $C_{20}H_{17}NO_2$: C, 79.18; H, 5.65; N, 4.62. Found: C, 79.62; H, 5.59; N, 4.64. Isomer B. Found: C, 78.82; H, 5.52.

12-Methylol-9,10-ethanoanthracene-12-carboxylic Acid and Lactone.—A mixture of 0.45 g. (0.0015 mole) of 9-cyano-9,10-ethanoanthracene-12-methylol acetate and 0.6 g. (0.011 mole) of potassium hydroxide in 7 ml. of ethylene glycol was heated at 125–130° for 22 hours. The cooled reaction mixture was acidified with 50% hydrochloric acid and extracted with five 25-ml. portions of ether. The combined ether solutions were then extracted with five 25-ml. portions of 5% sodium bicarbonate solution. The light yellow sodium bicarbonate solution was acidified with 10 ml. of concentrated hydrochloric acid, and 0.19 g. of a white precipitate formed, m.p. 216–219°. The long white needles which formed after recrystallization from aqueous ethanol had a double melting point. At 155° the material melted quite sharply, but upon continued heating it resolidified and melted again at 222–223°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.61; H, 5.55.

The ether solution containing the neutral fraction was evaporated to dryness leaving 0.173 g. of residue, melting at 194–200°, which upon recrystallization gave a melting point of 215–218° and proved to be identical with the compound formed by heating the acidic fraction.

The analytical sample of 12-methylol-9,10-ethanoanthracene-9-carboxylic acid lactone melted at 222–223°.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.54; H, 5.44.

9,12-Dicyano- and 9,11-Dicyano-9,10-ethanoanthracene.—A mixture of 4.00 g. (0.0197 mole) of 9-cyanoanthracene, 20 ml. (0.307 mole) of acrylonitrile and 0.1 g. of hydroquinone was heated in a sealed tube for 18 hours at 135–145°. Upon cooling, the material in the unopened tube solidified into a large mass of yellow needles. Since this indicated unreacted 9-cyanoanthracene was present the tube was heated for 22 hours more at 190–200°. This time when the tube was cooled, no yellow crystals appeared. The excess acrylonitrile was evaporated, and the residue was dissolved in methanol and the solvent allowed to evaporate slowly. Two types of crystals were formed in this process: a white, fine grained, agglomerate which melted at 196–198° in crude form, and large beautiful prismatic crystals of slightly yellow color, m.p. 165–166°, weighing as much as 0.125 g. each. By a process of separating the crystals manually and by recrystallization from methanol, 1.70 g. (33%) of the crystals melting at 204–205° (the 9,11-dicyano) and 0.95 g. (18.5%) of white crystals melting at 166.5–167.5° (the 9,12-dicyano) were obtained.

Anal. 9,11-Dicyano isomer. Calcd. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72; N, 10.93. Found: C, 84.40; H, 4.85; N, 10.76. 9,12-Dicyano isomer: Found: C, 84.40; H, 4.77; N, 10.78.

In a second run 3.5 g. (0.0173 mole) of 9-cyanoanthracene, 30 ml. (0.46 mole) of acrylonitrile and 0.1 g. of hydroquinone were heated in a sealed tube for 23 hours at 190–200°. Upon evaporation of excess acrylonitrile a light tan residue remained. Treatment as before led to 0.36 g. (8.1%) of the 9,12-dicyano isomer, m.p. 166.5–167.5°, and 0.75 g. (16.9%) of the 9,11-dicyano isomer, m.p. 204–205°.

A mixture of 0.274 g. (0.001 mole) of the adduct of 9-cyanoanthracene and acrylamide, m.p. 216–219°, and 10 ml. of acetic anhydride was refluxed for one hour. The addition of 2–3 ml. of water and cooling gave 0.167 g. (65%) of product, m.p. 163–164°. A mixed melting point with the lower melting dinitrile showed no depression.

Two grams of 12-cyano-9,10-ethanoanthracene-9-carboxaldehyde,[2] 2 g. of hydroxylamine hydrochloride, 10 ml. of ethanol and 10 ml. of water were refluxed for two hours, cooled and dried with an air jet. After extraction with water the residue was recrystallized from aqueous methanol and 1.26 g. of oxime, m.p. 196–197°, was obtained. Repeated recrystallization gave an analytical sample melting at 206–207°.

Anal. Calcd. for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.62; H, 5.04; N, 10.19.

When this oxime was dehydrated with acetic anhydride the product was found to be identical with the lower melting adduct of 9-cyanoanthracene and acrylonitrile prepared above.

Hydrolysis of 9,12- and 9,11-Dicyano-9,10-ethanoanthracene.—The lower melting isomer was hydrolyzed by heating 0.71 g. in 15 ml. of ethylene glycol with 1.12 g. of potassium hydroxide for 40 hours at 150°. The product was recrystallized from aqueous methanol after acidification and 0.75 g. (92%) of solid, which first started to melt at 224° and was completely melted at 230–231°, was recovered. Mixed melting with the 9,12-dicarboxylic acid previously obtained from the acrylamide adduct showed no depression. After drying over phosphorus pentoxide at 120° the neutralization equivalent was 150, calcd. 147.

When 0.80 g. of the higher melting dicyano isomer was hydrolyzed 0.44 g. (47%) of an acid melting at 268–270° was obtained, lit. 266–268°.[4]

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79. Found: C, 73.28; H, 4.93.

Acknowledgment.—Carbon–hydrogen analyses were performed by Galbraith Microanalytical Laboratories and Microchemical Specialties. Nitrogen analyses were done by Mrs. D. E. Ramey. The acrylamide was a gift of the American Cyanamid Co. and the acrylic acid a gift of the B. F Goodrich Chemical Co.

BOULDER, COLORADO

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Synthesis of Branched Primary and Secondary Alkyl Acetates

BY SHALOM SAREL[1] AND MELVIN S. NEWMAN

RECEIVED JUNE 25, 1956

The preparation and properties of a number of highly branched primary and secondary alcohols and of the corresponding acetates are described.

In connection with the study of the rates of alkaline hydrolysis of acetates of branched alcohols in the accompanying paper it was necessary to prepare the required esters. This paper describes the methods of preparation and properties of the necessary compounds.

All of the primary alcohols were prepared by the reduction of acids or esters with lithium aluminum hydride. In general the yield was better when the free acid rather than the methy or ethyl ester was used.[2] For example, only a 65% yield of pure neopentyl alcohol was obtained on reduction of ethyl trimethylacetate whereas reduction of the acid afforded the desired alcohol in 92% yield.

Reduction of hindered acids or esters was quite sluggish and often incomplete. For example, after 8 hours of reflux with excess reagent triethylacetic acid was reduced in only 65% yield and 25% of acid was recovered. Similarly after 12 hours diisopropylacetic acid was reduced in 86% yield and 10% of acid was recovered (see Table I for the other data).

The more highly hindered acids were made by three methods: (1) alkylation of acetonitrile followed by hydrolysis,[3] (2) alkylation of ethyl cyano-

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[1] Formerly Shalom Israelashvili. The work herein reported was supported by a grant from the Office of Naval Research.

[2] See J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2515 (1951).

[3] (a) K. Ziegler and H. Ohlinger, *Ann.*, **495**, 84 (1932); (b) N. Sperber, D. Papa and E. Schwenk, THIS JOURNAL, **70**, 3091 (1948); (c) C. Schuerch, Jr., and E. H. Huntress, *ibid.*, **70**, 2824 (1948).